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Coral Bay Shore Zones Tar Ball Distribution

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Abstract

Oil spill and wastewater discharge to the marine waters contribute to the tar ball formation after the residue washout to the sandy beaches. The oil degrades over time through dynamic changes of the hydrocarbon compounds once exposed to the environmental factors which influences the fate and transport of the oil residue. Tar balls collected from Coral Bay shore zone which is used for recreational activities are 100 gm/strip with up to 6 cm in diameter. The collected tar ball was analyzed using FID gas chromatography after 50% n-hexane and dichloromethane extraction and fingerprint to the diesel and crude oils. The tar ball sample contains beta-pregnane (22-29 %) and dotriacontane (52-68 %) which accumulate over long time from crude oil spills in the Strait of Malacca.

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Keywords: Tar ball; hydrocarbons; marine waters

1. Introduction

This paper investigates the hydrocarbons residues spillage that forms the tar ball deposit on the shore zones at the Coral Bay located at Pangkor Island. The hydrocarbon fate and transport drives by the biodegradation and photolysis, and mixing accelerated by the environmental factors of wind speed and currents. The oil slick washed off to the shore zones coagulated with sandy particles and debris forming the ubiquitous tar ball from resistant hydrocarbons compounds.

Nomenclature

χ	Particle dispersion, dimensionless
u	Speed of fluids (cm/s)
T	Time (min)
L	Langmuir Cell dimension (m)

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1.1. Oil pollution

Hydrocarbon resources had been drilled and utilized by mankind from the nineteenth century. The discovery leads to the utilization of fossil fuel to assist human activities. Global fuel consumption of 1.0 million bbl/d was recorded for 2013 but the consumption was decline in 2014 [1]. The fuel products are utilized in motor vehicles, power generators and jet fuels. The massive production and uses of fuels create oil pollution to the environment. Typical crude oil contains 58% saturates, 28.6% aromatics, and 14.2% polar compounds. CH_2 is found dominance the saturated molecules components. The oil spill or oily residue is a complex combination of refined products, additives, silica, metals and heavy tars.

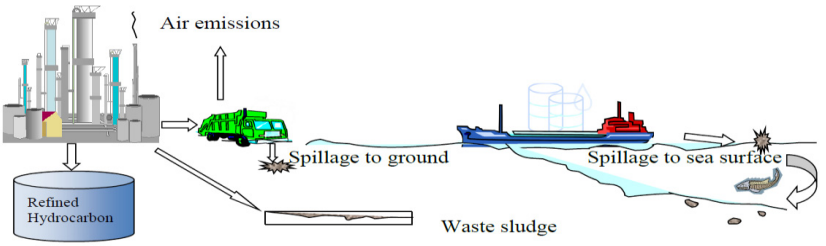


Fig. 1. Hydrocarbon spillage and migration.

Critical environmental damage occurs in the case of crude oil spillage, from process stream or during transport as in Figure 1. The incident is caused by human error or system error during operation or natural disaster such as heavy storm and earth quake. Table 1 shows the normal release of petroleum products to the environment.

Table 1. Hydrocarbon release into the environment.

Sources	Cases
Tankers	Oil water mixtures remaining in tanks are discharges into the environment
Tankers accidents	structural failure, followed by grounding and collisions
Dry docking	Tankers must be cleaned during maintenance and inspection
Terminal operations	Losses from spillage in transfer
Bilges and bunkering	Bilge water and leaks from bunkers
The atmosphere	Internal combustion engines and power plants
Municipal and industrial wastes	Sewage-treatment plants and industrial wastewater
Urban runoff	Oil heating system, automobiles, and service stations
Point sources	Power plants, military bases, and marinas
Storage facilities	Gasoline and jet fuel tanks, military fuel depots

Major oil spill incidents create expensive lesson learned as shown by the former cases:

- *The Florida* spill of nearly 700,000 L of oil resulted in 15 cm deep of oil in sediment. The oil spill is remains in the same condition in 1976, after 7 years of the cases as found by the scientist.
- Estimated 200,000 tonnes fuel oil spill from *Prestige* caused more than 200 million Euros been spent for beach cleaning so far.
- Exxon spent more than $2 billion cleaning up 34,000 tonnes of crude oil spilled in 1989 Exxon Valdez disaster in Alaska.
- Estimated damage of 1999 disaster off the French coast from the tanker *Erika* spilling of 15,000 tonnes of fuel oil, had cost as high as $860 million.
- Brazil state oil Petrobras had appeal a $180 million court award to fisherman following a major oil spill in Rio De Janeiro's scenic bay in Jan 2002.

Strait of Melaka is one of the important marine water for navigation in the South East Asia region. According to DOE Environmental Quality Reports, oil and grease is the highest pollutant to Malaysians marine water. The Environmental Quality Reports 1995 to 1997 the oil and grease contributed to 60 to 85 % compare to the other marine water pollutants [2, 3, 4]. The

Straits of Malacca recorded significant oil and grease content which degrade the marine waters quality. Table 2 shows Straits of Malacca oil spill incidents cases.

Table 2. Oil spills in the Straits of Malacca.

Sources	Location	Cause	Quantity (tonnes)
Jul 24, 1976	102d 56m E, 1d 32m N	Vessel accident	5500
May 16, 1977	Tanjung Keling	Vessel pipeline rupture	60
Aug 13, 1978	102d 9m E, 2d 13m N	Oily water discharge	5-10 gallon
Jan 20, 1980	Port Klang	Pipe leak from vessel	2-3 drum
Sept 20, 1981	Shell Refinery PD	Valve leak from vessel	1037
Oct 21, 1981	Port Klang	Wrong valve open from vessel	200 gallon
May 29, 1984	Port Klang	Vessel leaking	1350 gallon
Jul 26, 1986	Esso Depot, Penang	Depot pipe leaking	>2 barrel
Dec 17, 1987	Esso Jetty, PD	Vessel	200 liter
Mac 23, 1988	Esso Plant, Port Klang	Plant	180 gallon
Oct 15, 1989	Esso Refinery	Transfer overflow from vessel	80 liter
Oct 18, 1989	Port Dickson	Pipe leaking	18 gallon
Dec 4, 1989	Shell Refinery	Refinery overflow	200
Aug 16, 1990	South West of Johore	Tanker cleaning from vessel	4000
Sep 20, 1992	East of Ujong Temiang	Collision of vessel	13000

1.2. Hydrocarbons fate and transport

The spilled oil spread on the surface water forming a thin film of oil slick. Oil composition in the slick degrade when exposure to high temperature and water properties which influence the degradation processes (Figure 2). Light fractions will evaporate, water-soluble components dissolve in water and immiscible components become emulsified and dispersed as a small droplet, also form chocolate mousse. Floating slick can absorb 20-80 % waters.

Initially the oil spread based on gravity over water surface mobilized by wind and current which extend up to weeks. The spill evaporates almost half of the compound containing carbon 13 to 14 after 24 hours. Oil mix with water forming oil-in-water emulsion subjected to current dispersion and turbulence which differs from water-in-oil emulsion forming stable thick chocolate mousse with reduced oil loss to the environment. The water-in-oil emulsion are resulted from the accumulation of resin and asphaltene that form a barrier to recoalescence [5]. Vertical dispersion is constrained by the presence of boundaries and stratified layers and immediately achieved in well mixed conditions while horizontal dispersion govern by the environment dispersion coefficient estimates by physical length scale of the dispersing motion and velocity scale of the motions [6]. The Langmuir cell, the wind driven shear instability affects vertical dispersion of oil droplets move down the water column. Langmuir cell is described by the speed of fluid, u (cm/s) depends on the wind speed, cell dimension, L (m) and duration time, T (min) that affect particle dispersion, χ as in Equation 1. In general crude oil (CH_2O) were oxidized to CO_2 and water as in Equation 2. Hydrocarbon derivative include alcohols ketones and organic acids whereby molecules with 20 carbons and less are oxidized before the larger ones in the order of n-alkanes, branched and cyclic alkanes, polycyclic aliphatic and aromatic.

$$\chi = \frac{uT}{L} \tag{1}$$

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{2}$$

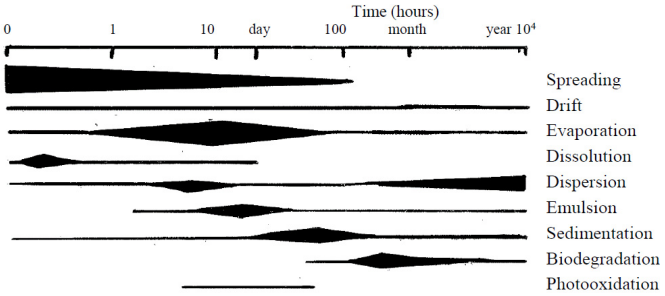


Fig. 2. Processes and timescale involved in the breakdown of an oil slick.

The stabilized crude oil washed off on shorelines will coagulated with the sand and debris formed tar ball. The oil slick float on sea water surface moves in downwind direction at the rate of 3% of the wind speed before stranded on the shore zone. The tar ball sampling were conducted based on concentration in g/m^2 or volume of oil within each segment or strip [7]. The tar ball create aesthetical issues to the recreational facility due to their long term persistence and ubiquitous nature. The sampling of tar ball in the Coral Bay shores was conducted to trace the sources of hydrocarbon spillage and identify the main component in the residue.

2. Methodology

2.1. Sample collection

Tar balls sampling were conducted at Pangkor Island, a tourism spot, 12 km from the Jetty of Lumut. The tar balls were collected along the west coast of Pangkor Island, at 600 meters of Coral Bay stretches as shown in Figure 3. Insignificant tar balls can be found on Teluk Nipah, Turtle bay or Pasir Bongak shore zones. Geographically, Coral Bay shorelines are prone to trap wash off residue as shown by significant tar balls distribution in the sampling areas. The collected tar balls along Coral Bay shore zones recorded up to 100 gm/strip. A strip of sampling area forms a square meter beach zone. Previous Malaysian DOE tar balls records from various sampling stations indicated that the range are 18.2 gm/strip at Telok Mahkota, Johore to 1110.0 gm/strip at Tanjung Rhu, Langkawi [8], Coral Beach has moderately low amount of tar balls deposit. Historically, the Coral Bay tar balls were originated from Port Klang vessel oil spill in 1988. Even though, cleaned-up program was initiated to remove the oil slick, the oil residue continuously accumulated from the recent marine activities discharges and spillage by the Northeast wind shoreline stranding from April to September. The tar balls can be visually inspected by the black in colour heteregenous surface balls scattered on the shorelines blended with sand, gravel and soil particles in 2 to 6 cm diameter.

Fig. 3. Tar ball sampling area on the Coral Bay [9]

The tar balls distribution on the beach is affected by the wind speed and wind direction, and the concentration may change at any one time or location which would be expected to vary with changes in tidal or wind-induced water levels or in response to sediment redistribution [10]. High distribution of tar balls will affect people acceptability to recreational activity in term of cleanliness and visibility. Corbin et al., [11] classify the tar balls accumulation on the beach zone into four different perceptions as given in Table 4. Coral Bay is classified as moderate perception toward acceptations by the beach user.

Table 4. Tar ball classification [10]

Tar ball volume (g/m)	Perception
0 – 1.0	Negligible
1 – 10.0	Low background
10 – 100.0	Moderate
> 100	Highly unsuitable for recreational purposes

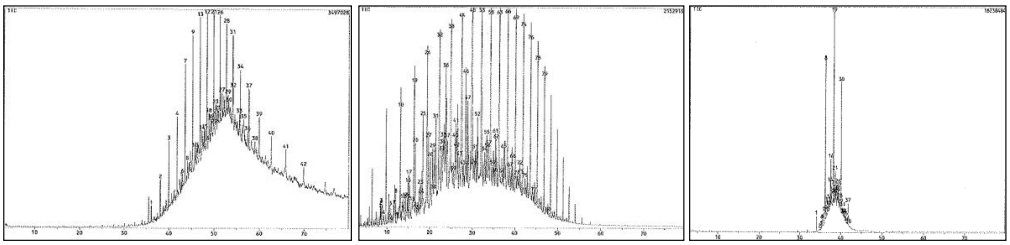
2.2. Sample analysis

The collected samples were washed and dry with sodium thiosulphate before extracted by 50 % hexane and dichloromethane solution for 8 hours and concentrated to 1 ml. 3 µL of sample was injected to DB-5 fused silica capillary column of 0.25 mm diameter x 30 m length at initial temperature of 100°C with 8 °C/min ramp to 280 °C using FID gas chromatography. Weathered tar ball sample chromatogram was compared with diesel oil and crude oil chromatograms to trace the nature and sources of the oil residue through fingerprinting or pattern recognition.

3. Results and Discussion

3.1. Tar ball analysis

The collected tar balls were divided into four sample areas for organic content identification and replicates analysis were conducted for each sample points. Due to the heterogeneous nature of the sample, the chromatograms of extracted tar balls have different hydrocarbon distribution but dominant components in the tar ball resemble crude oil chromatograms as in Figure 4.



(a) (b) (c)

Fig. 4. Chromatograms of (a) tar ball (b) diesel oil (c) crude oil.

The tar ball sample contain mainly heavy compound of dotriacontane, $C_{32}H_{66}$ (from 52-68 %) and beta-pregnane, $C_{21}H_{36}$ (22-29 %) in all samples (Figure 5a). Other hydrocarbons found in smaller percentage are hexadecanol, 1-chloro octadecane and pentatriacontane compounds. While the diesel and crude oils show average distribution of compounds with crude oil also contain beta-pregnane and dotriacontane of 15.84 % and 14.68 % (Figure 5b) accordingly of which the tar ball most probably accumulate over time which originally crude oil spill from tankers from strait of Malacca. Hydrocarbon compounds with 20 carbon atoms and above are considered as resistant to biodegradation in the environment.

Dotriacontane is a linear family of alkanes becomes the most stable and abundant compound in the tar ball while the beta-pregnane is the parent hydrocarbon consist of cyclohexanes and cyclopentane with alkyl substitution which may act as biomarkers to most of biomaterial sources and also used as steroids.

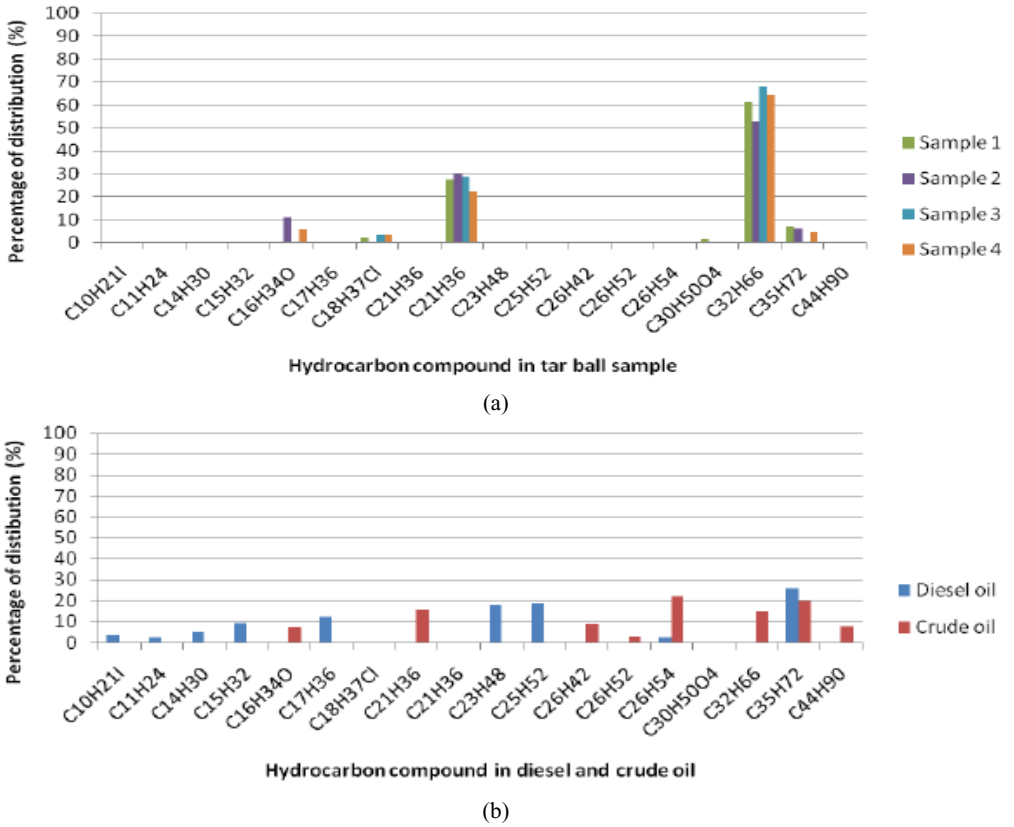


Fig. 5. Hydrocarbon compounds in (a) tar ball and (b) diesel and crude oil.

3.2 Control mechanisms

The practicable methods for oil spillage and oily wastewater discharges prevention and minimization can be achieved by effective legal enforcement and control strategies. The inventions of dispersant, sorbent and cleaning agents are able to remove oil residue from marine waters in combination with mechanical means to optimize the oil spill cleaning.

Legal requirements and enforcement are successful approach to prevent and control oil pollution by the government authorities. Environment Quality Act 1974, Amendment 1985 [12] is one of the comprehensive laws to control oil pollution and wastewater discharges. The clause in Section 26 prohibit any person from discharging or spilling oil outside the territorial waters of Malaysia if such discharges or spills would results in the oil being washed into Malaysian waters. Under the Section 27, which originally prohibits the discharge of oil into Malaysia water was amended in 1985 to prohibit any discharge of oil in contravention of acceptance conditions, unless licensed in which a penalty will be issued. Provision to control pollution in the marine waters include (i) Merchant Shipping (Amendment and Extension) Act 2011 [13] for offshore installation (ii) Continental shelf Act 1966 (revised 1972) [14] for territorial waters (iii) Petroleum Mining Act, 1966 (revised 1972) [15] for effluent in the vicinity of the exploration area (iv) Exclusive Economic Zone Act 1984 [16] for 200 miles off the territorial waters of Malaysia. Merchant Shipping (Oil Pollution) Act 1994 (Amendment 2005)[17] feed from Convention of Civil Liability for Oil Pollution Damage 1969 and International Conference for Oil Pollution Damage 1971 is one of important acts that emphasize on the polluters pay principles through liability Fund. The international frameworks for combating major oil pollution incidents include the Oil Pollution Preparedness, Response and Cooperation 1990 and Civil Liability Convention 1992 which require preparation of contingency plans until tiers 3 responses, established and supported by the industry stakeholders.

Bioremediation of the oil spill and oil contamination was preferred in many cases for the effective and practical treatment which consider as safe and less environmental impacts [18-21]. The microbial culture bioremediation agents includes BET BIOPETRO, RESTORATION MICRO-BLAZE, OPPENHEIMER formula, PRISTINE SEA II, STEP ONE, SYSTEM E.T. 20 and WMI-2000 can be used. Nutrient support bioremediation agents are BILGEPRO, INIPOL EAP 22, LAND AND SEA, VB591RTMWATER, VB997TMSOIL and BINUTRIX [22]. In-situ aquifer uses soil microbes with aid of nutrient and oxygen by direct underground injection. Excavated contaminated soil use forced aeration system to remediate contaminants, while

dissolved aromatic hydrocarbon is treated by anaerobic nitrification. Mechanical methods like fence, shore-sealing or curtain booms for containment, deflection or site protection is recommended [23], slick-lickers and others mechanical devices for fast cleaning of oil at sea water surface can be installed by the oil spill owner. Oil emulsion spray will forms chocolate mousse using helicopter e.g. polyurethane foam significantly enhance the cleaning process. Mulching technique reduces BOD, COD, fat, oil and grease into CO_2 and water. Hegrem, an effective commercial product for oil spill cleaning available at low cost using simple technology promotes natural attenuation or biostimulation. The method provides extra oil-degrading bacteria of its own known as bioaugmentation. It consists of waste plant fibers and powdered nut shells, with enhance sorbent capacity while retain and immobilize oil without leaching.

4. Conclusions

The tar ball accumulate over long period of times resulted from incidental spillage collected from Coral Bay shore zones of 100 gm/strip is classify as medium perception which render aesthetical value for recreational activities. Beta-pregnane, $C_{22}H_{36}$ and dotriacontane $C_{32}H_{66}$ form about 85 % of tar ball hydrocarbon compounds. The tar ball chromatogram resemble crude oil pattern which indicate the spill were originated from previous crude oil spillage occurred in the Strait of Malacca from shipping routes. Continuous effort to clean oil spill and the residues are possible through legal requirements and enforcement, mechanical or bioremediation methods to maintain the beach cleanliness and prevent contamination of the marine waters and soil.

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